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Photochemical Response of Electronically Reconfigurable Molecular-Based Switching Tunnel Junctions

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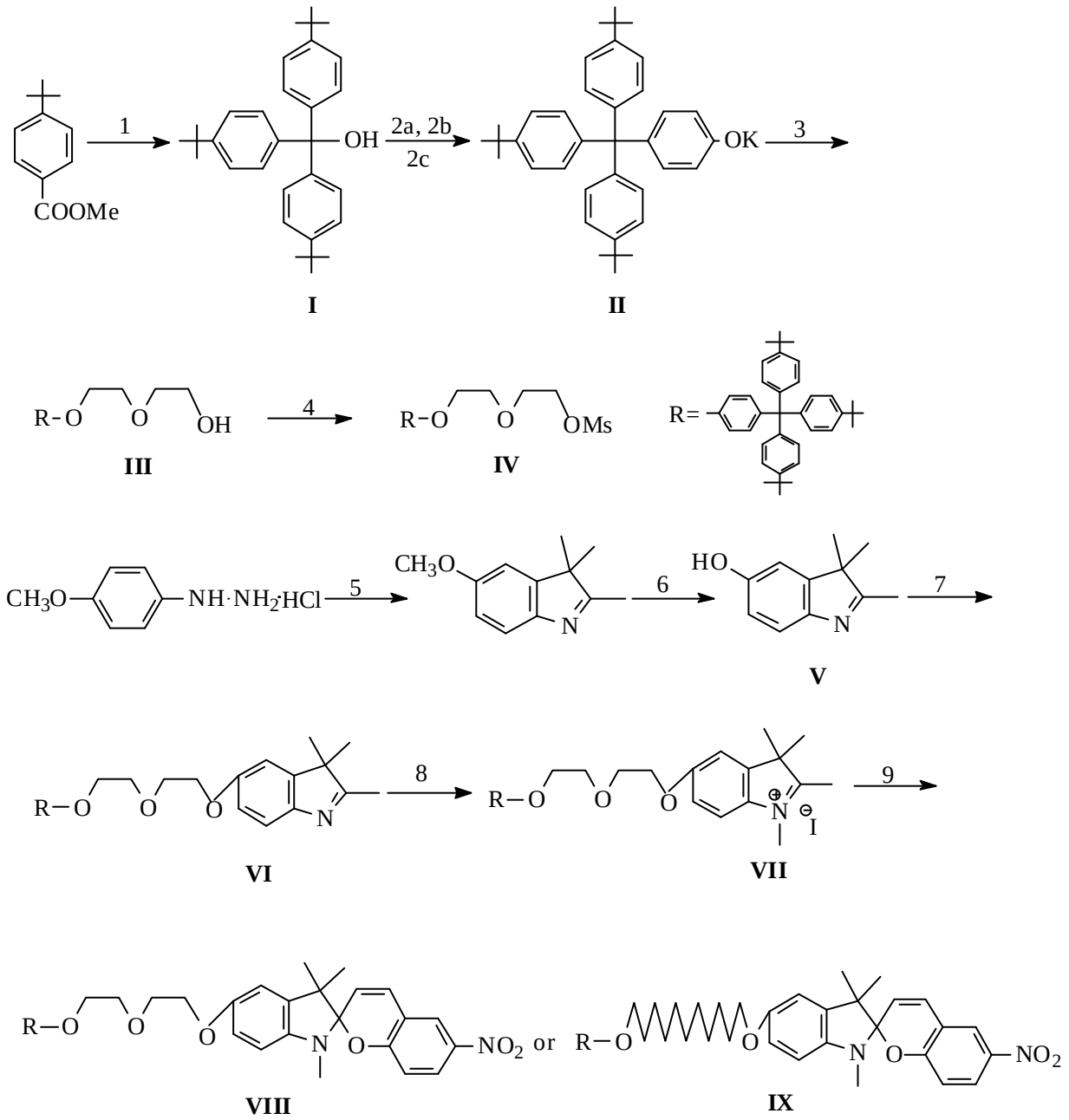

Scheme 1: 1) THF, 4-*tert*-Butylphenylmagnesium bromide, 70 %; 2) 2a: Acetyl Chloride, 24 h; 2b:Phenol,100^{o}C, 24 h, 95%. 2c: 40% KOH. 3) 2-(2-Chloroethoxyl)ethanol, MeCN, K_2CO_3, KI, 4 days, 70%; 4) TEA/CH_2Cl_2, CH_3SO_2Cl,-5 ^{o}C, 94%. 5) Ethanol, 4-Methoxyphenyl-hydrazine hydrochloride, methyl isopropyl ketone, 4 h; 6) BBr_3/CH_2Cl_2, -0 ^{o}C, RT 12 h, 90%.7) Compound **IV**, MeCN, K_2CO_3, 48 h, 67 %; 8) MeI/CH_2Cl_2, 10 h, 100%; 9) 2-Hydroxy-5-nitro-benzaldehyde/2-butanone, piperidine, 2 h, 88%.

Experimental Section

NMR spectra were recorded on a 360 MHz Bruker AM-360 NMR spectrometer with ^1H spectra recorded at 360 MHz using TMS (δ=0.00 ppm) as internal reference. Absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer. All starting materials used in the following experiments were purchased from Aldrich Chemical Company and used without further purification. Elemental analyses were performed by Desert Analytics, Tucson, Arizona. Mass spectra were obtained using the FAB technique. Cyclic voltammograms (CV) were recorded on a BAS 100B/W Electrochemical Workstation using a "micro electrode" (μCV) of in-house design.[1] The electrochemical cell was composed of a Pt disc (BAS) as working electrode, Pt ring as counter electrode (auxiliary electrode) and Ag/AgCl wire (prepared by oxidizing a silver wire in aqueous NaCl solution) as reference electrode. Electrolyte solutions were prepared by dissolving 0.1 M Bu_4NPF_6 in anhydrous acetonitrile. Sample solutions were prepared by dissolving a very small amount of the sample in about 100 μl electrolyte solution. A small amount of ferrocene was added for internal reference. Electrolyte and sample solutions were prepared in the drybox. All CV measurements were performed in a drybox.

Synthesis

Potassium 4-[4-Tris(*p-tert*-butylphenyl)methyl]phenolate II: Compound **II** was synthesized in three steps according to literature procedures.[1]

Tris(*p-tert*-butylphenyl)methanol I: To a solution of 25 mL (~ 50 mmol) of 4-*tert*-butylphenyl magnesium bromide (2 M in ether) in 85 mL THF was added dropwise 4.58 g (~ 23.8 mmol) of methyl 4-*tert*-butylbenzoate in 10 mL THF over 30 min. After addition, the mixture was refluxed under nitrogen for ~ 18 h. The solution was cooled down to room temperature and neutralized with 10% HCl. The reaction mixture was extracted with hexane. The combined hexane extracts were washed with water three times and dried with $MgSO_4$. A white solid,

tris(*p-tert*-butylphenyl)methanol, 7 g (~ 70%) was obtained after removal of solvent and recrystalization from ethanol. ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 27H, CH_3), 7.27-7.35 (m, 12H, arom).

Potassium 4-[4-Tris(*p-tert*-butylphenyl)methyl]phenolate II: (2a): Compound **I** (3.2g, 7.47 mmol) was dissolved in 15 mL acetyl chloride and refluxed for 18 hours. The reaction mixture was then cooled and excess acetyl chloride was removed by aspirator vacuum. A light creamy yellow viscous liquid was obtained. The crude product, without purification, was converted to (*p*-hydroxyphenyl)tris(*p-tert*-butylphenyl)methane by reaction with phenol. Phenol, 7.1 g (75.4 mmol) was added into the crude product and heated at 100 ^{o}C for 24 h. Upon addition of phenol, the reaction mixture turned dark red, which solidified after 1 h. The reaction mixture was cooled down after 24 h, and stirred with 400 mL of hot 40 % aqueous KOH solution to remove phenol. The mixture was then filtered and washed thoroughly with water to yield 3.7 g (~89%) of white solid potassium 4-[4-Tris(*p-tert*-butylphenyl)methyl]phenolate (**II**) was obtained after drying under vacuum. ^{1}H NMR ($CDCl_3$): δ 1.30 (s. 27H), 6.70 (d, 2H, J=8.8 Hz), 7.03-7.09 (m, 8H), 7.22-7.24 (m, 6H).

Compound IV was synthesized by a literature procedures[2,3]: Compound **II** (5.8 g, 10.7 mmol), was added to a mixture of dry MeCN (65 ml), K_2CO_3 (1.5 g), KI (1.8 g), and 2-(2-chloroethoxyl)ethanol (1.3 g, 10.7 mmol). The reaction mixture was heated to reflux for 3.5 days. A white solid, 4.4 g (70%) of **III** was obtained after flash chromatography (eluent ethyl acetate/hexane, 1:1.9). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 27H), 3.66-3.68 (m, 2H), 3.73-3.77 (m, 2H), 3.85-3.87 (m, 2H), 4.10-4.13 (m, 2H), 6.78 (d, 2H, J=8.8 Hz), 7.06-7.10 (m, 8H), 7.21-7.24 (m, 6H). To a solution of compound **III** 4.4 g (7.4 mmol) in CH_2Cl_2 (55 mL) was added triethylamine (16 mmol) at –10 ^{o}C, followed by addition of ~ 0.7 mL (9 mmol) of

methanesulfonyl chloride dropwise at – 10 ^{o}C. Stirring for 30 min completed the reaction. The reaction mixture was transferred to a separatory funnel, washed with ice water, followed by cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. The methylene chloride solution was dried with $MgSO_4$ and upon solvent removal gave the product **IV** (94%). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 27H), 3.04 (s, 3H), 3.82-3.87 (m, 4H), 4.09-4.12 (m, 2H), 4.39-4.41(m, 2H), 6.75 (d, 2H, J=8.8 Hz), 7.05-7.10 (m, 8H), 7.21-7.24 (m, 6H).

5-Hydroxy-2,3,3,-trimethyl indolenine V: Compound **V** was synthesized in two steps according to the literature.[4,5] A solution of 4-methyoxyphenylhydrazine hydrochloride (10 g, 0.057 mmol), 3-methyl-2-butanone, and absolute ethanol was heated at reflux for 4 h. After filtration the solvent was removed to give the 5-methoxy-2,3,3,-trimethyl indolenine. The crude compound without further purification was used directly for the synthesis of compound **V**. A solution of 5-methoxy-2,3,3-trimethyl indolenine (0.057 mmol) in 30 mL CH_2Cl_2 was cooled down to –10 ^{o}C and treated with BBr_3 (11 ml, 0.11 mol) in 20 mL CH_2Cl_2 dropwise. After addition, the reaction mixture was warmed to room temperature overnight and neutralized carefully with saturated sodium carbonate. The CH_2Cl_2 organic phase was separated and dried. Evaporation of solvent yield product **V** (8.7 g, ~ 90%). ^{1}H NMR ($CDCl_3$): 1.29 (s, 6H), 2.27 (s, 3H), 6.78 (dd, 1H, J=8.3 Hz), 6.85 (d, 1H, J=2.4 Hz), 7.32 (d, 1H, J=8.3 Hz).

Compound VI: To a solution of 0.3 g (1.7 mmol) of 5-hydroxy-2,3,3-trimethyl indolenine in a solvent mixture of 15 mL dry MeCN and 5 mL acetone was added 0.46 g of K_2CO_3 while stirring, then 1 g (1.5 mmol) mesylate **IV** was added in portions and the reaction mixture was heated at reflux for 48 h. The crude mixture was purified by flash chromatography (eluent ethyl acetate/hexane, 1:2). A light yellow solid 0.75 g (67%) was obtained. FABMS (M^{+}): 749.5; ^{1}H NMR ($CDCl_3$): δ 1.27-1.30 (m, 33H), 2.30 (s, 3H), 3.91-3.95 (m, 4H), 4.12-4.18 (m, 4H), 4.10-

4.13 (m, 2H), 6.78 (d, 2H, J=8.8 Hz), 6.84 (dd, 1H, J=8.4 Hz), 6.90 (d, 1H, J= 2.4 Hz), 7.06-7.09 (m, 8H), 7.21-7.24 (m, 6H), 7.46 (d, 1H, J=8.4 Hz).

Compound VII: Compound **VI** (0.75 g) was dissolved in ~ 5 mL CH_2Cl_2 and ~ 1 mL MeI was added.[6] The reaction mixture was refluxed for 12 h. Solvent evaporation of the mixture gave ~1.15 g solid compound **VII** (97%). ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 27H), 1.61 (s, 6H), 3.03 (s, 3H), 3.91-3.97 (m, 4H), 4.12-4.15 (m, 2H), 4.22-4.24 (m, 2H+3H), 6.78 (d, 2H, J=8.9 Hz), 7.08-7.10 (m, 8H+2H), 7.21-7.24 (m, 6H), 7.54 (d, 1H, J=8.7 Hz).

Compound VIII: The iodide salt **VII (**600 mg, 0.67 mmol) and 2-hydroxyl-5-nitro-benzaldehyde (120 mg, 0.71 mmol) were dissolved in ~5 mL of 2-butanone in the presence of 68 μl (0.69 mmol) of piperidine.[5] After the reaction mixture was refluxed for 2 h, the solvent was evaporated. The material was purified via flash chromatography (eluent ethyl acetate/hexane, 1:5.6). A greenish solid **VIII**, (540 mg, 88%) was obtained, which is the spiropyran derivative and shows reversible photochromic properties based on its absorption spectra. FABMS (M^+): 912.6; ^{1}H NMR ($CDCl_3$): δ 1.17-1.30 (m, 33H), 2.67 (s, 3H), 3.91-3.94 (m, 4H), 4.09-4.15 (m, 4H), 5.83 (d, 1H, J=10.4 Hz), 6.43 (d, 1H, J=8.3 Hz), 6.71-6.80 (m, 2H+3H), 6.89 (d, 1H, J=10.3 Hz), 7.07-7.10 (m, 8H), 7.21-7.23 (m, 6H), 7.98-8.00 (m, 2H). Anal. Calcd. for $C_{60}H_{68}N_2O_6$: C, 78.92; H, 7.51; N, 3.06. Found: C, 77.30; H, 7.51; N, 2.99.

Compound IX: This spiropyran derivative was synthesized in a similar fashion as the procedure described above. The only difference was in step 3, where compound **III** was made. Instead of using 2-(2-chloroethoxyl)ethanol, 11-Bromo-undecanol was added to allow reaction with the potassium phenolate salt **II** under the same conditions for 48 h. The product was purified by recrystalization from ethanol instead of flash chromatography. Compound **IX** was a light yellow solid with photochromic properties similar to those of compound **VIII**. FABMS (M^+): xxx . ^{1}H

NMR ($CDCl_3$): δ 1.24-1.47 (m, 41H), 1.73-1.78 (m, 4H), 2.68 (s, 3H), 3.92 (*t*, 4H, J=6.5 Hz), 5.85 (d, 1H, J=10.4 Hz), 6.45 (d, 1H, J=8.0 Hz), 6.71-6.78 (m, 2H+3H), 6.90 (d, 1H, J=10.4), 7.06-7.09 (m, 8H), 7.21-7.24 (m, 6H), 7.99-8.02 (m, 2H). Anal. Calcd. for $C_{67}H_{82}N_2O_5$: C, 80.85; H, 8.30; N, 2.81. Found: C, 79.60; H, 8.22; N, 2.45.

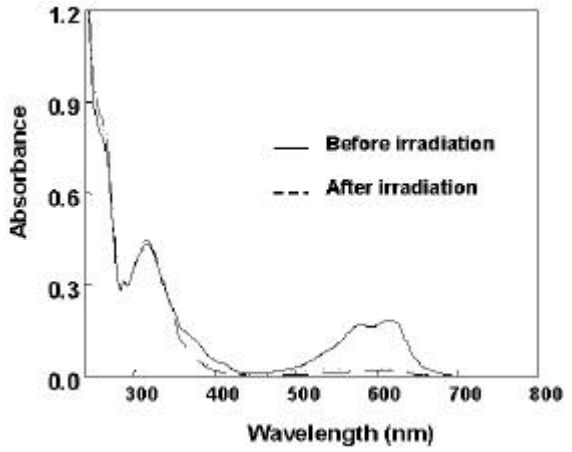

Figure S1. Absorption spectra of compound **IX** in hexane before and after 10 minutes of UV light irradiation.

Optical and Electrochemical Properties

The solutions of the spiropyrane derivatives **VIII** and **IX** in nonpolar solvents such as hexane are colorless. They only absorb UV light (< 400 nm). For example, the absorption spectrum of compound **IX** in hexane was recorded at room temperature and is displayed in **Figure S1**, which has an absorption peak maximum at ~ 316 nm**.** As observed in the past with photochromic spiropyran molecules,[6] the colorless hexane solution of compound **VIII** turned purple after irradiation of the light from an UV lamp for a few seconds. The absorption spectra of the colored species were recorded and are also shown in **Fig. S1.**. It can be seen that an additional new absorption peak around 615 nm grows in. The purple color of the irradiated solution disappeared after storage at room temperature for 10 min and eventually returned to the original colorless solution with the characteristic absorption spectrum of the spiropyran**.**. The process is fully reversible and the solution is stable. The cyclic voltammograms of the spiropyran compounds **VIII** and **IX** in anhydrous acetonitrile were measured in the presence and absence of UV light using a micro-cell (μCV) technique in a drybox. The nitro-substituted spiropyran derivatives basically have a reduction peak around –1.62 V (vs Ferrocene), which corresponds to

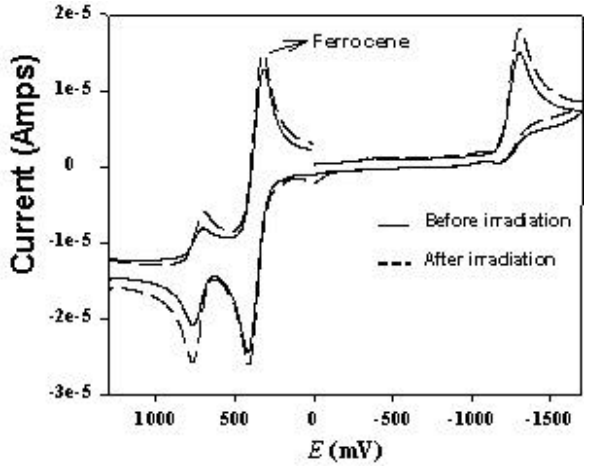

Figure S2. Cyclic Voltammograms of compound **IX** in 0.1 M Bu_4NPF_6 acetonitrile solution with ferrocene as internal standard before and after UV light irradiation.

the reduction of the nitro group,[7,8] and an irreversible oxidation peak at ~ 0.35 V that is a result of oxidation of nitrogen on the indolenine moiety[9] (**Fig. S2**). Similar to the general photochromic spiropyran compounds,[9] the CV of compounds **VIII** and **IX** show no meaningful difference with and without UV light, even thought the solutions turned dark purple color after irradiation (**Fig. S2**). It is likely that the quantum yield of the photocoloration of the spiropyran compounds is very low. This statement above is supported by the absorption spectra in Figure S1. The oscillator strength of the bands between 260 and 360 nm exhibit minimal changes upon irradiation with UV light. This implies that very little of the closed form is converted to open form and that the open form has a much larger absorptivity coefficient (560 -640 nm).

Langmuir-Blodgett Monolayers of Photochromic Compounds

Langmuir monolayers were prepared on 18.2 MΩ milli-Q water subphases using a NIMA Technology Type 611 Langmuir Trough using a spreading solvent of methylcyclohexane (MCH), purified according to standard literature procedures. This solvent was chosen because it is relatively nonpolar; the spiropyrans tend to more readily convert to the open merocyanine form in polar environments. To prevent light-induced conversion to the merocyanine form, all trough work was performed either in the dark, or under red light illumination using a Wratten filter (Kodak). Typically, 50 μL of 9 mM solutions of compound **1a** or **2a** in MCH were spread on the subphase, which was maintained at 25 °C. Before compression, the monolayers were

allowed to equilibrate for about 10 minutes. The monolayers were initially compressed at 10 cm^2/min. until the surface pressure began to increase, and then compressed at 2 cm^2/min. After obtaining the pressure-area (π-A) isotherms for each compound, LB monolayers were deposited at an area of roughly 75 $Å^2$/molecule onto clean, hydrophilic SiO_2 substrates patterned with 5 μm wide conductive n-doped (0.02 Ω-cm resistivity) smooth polycrystalline Si electrodes. Monolayers were transferred at a rate of 1 mm/min. on the upstroke at surface pressures just below where the surface compressibility began to decrease, which occurred at 20mN/m.

The fabrication of molecular sandwich tunneling junctions has been described previously.[10] In particular, the preparation of smooth poly-Si electrodes was a many step process, but was critical to achieving a high (effectively 100 %) device yield. Typically, poly-Si films formed via direct CVD growth onto SiO_2 are neither smooth nor defect free. However, amorphous silicon films can be very smooth.[11] Thus, low-pressure, SiH_4 CVD was used to deposit 1500 Å of amorphous Si onto 1100 Å of SiO_2 on a <100> silicon wafer at 525 °C. The film was exposed to air at room temperature for several minutes to form a passivating SiO_2 layer, and then crystallized under N_2 at 650 °C. Poly-Si films were implanted with 55 keV P^+ ions and 1 μm film of SiO_2 was grown by CVD to prevent out-gassing of the phosphorous. The dopant P atoms were activated at 1000 °C, and then a 6:1 mixture of NH_4F(aq):HF(aq) was used to etch away the SiO_2. Electrodes were patterned using photolithography. Following deposition of the LB film, 7 μm wide top electrodes (50 Å Ti followed by 1000 Å Al) were deposited using e-beam evaporation through a shadow mask.

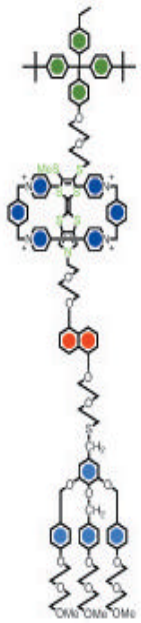

Figure S3. The [2]rotaxane molecule that was utilized as a control in this work. Several other molecular-mechanical systems were utilized as control molecules, as well as other, simpler molecules such as alkylcarboxylates and long-chain phosphatidic acids, and none of the devices containing those molecules exhibited any form of an optically-medicated response.

Devices were measured in air and at room temperature, using a manual probe station with coaxial probes. This probe station was enclosed in a light-tight, electrically grounded copper box. Current versus voltage (I/V) measurements were either made in the dark, or under red light illumination. Bias voltages were applied to the poly-Si electrode, and the top (Ti/Al) electrode was connected to ground through a DL Instruments 1211 current preamplifier.

A mineral lamp blacklight operating at the high-energy mode (λ<350nm) supplied the UV light, and a helium-neon laser at 632nm with an expanding and collimating lens set supplied the visible light for measuring the photochemical responses of the spiropyran junctions. Control measurements were performed on many devices, including tunnel junctions that incorporated LB monolayers of simple amphiphiles such as eicosanoic acid, more complex amphiphiles such as the molecular-mechanical complex shown in Figure S3. (the control data in Fig. 2 of the paper utilized a device fabricated from this molecule[12]), and devices with no molecular component at all. None of these devices exhibited any light-dependent changes in the tunnel current. In fact, of all of the molecular tunnel junctions that we have investigated, only the spiropyrans described here yielded an optically-driven response, and that response dominated the device characteristics.

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